A-UNIFAC Modeling of Binary and Multicomponent Phase Equilibria of Fatty Esters+Water+Methanol+Glycerol

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Abstract

The production of methyl and ethyl esters of fatty acids is of great industrial interest, considering the direct application of these esters as biodiesel. Prediction of the phase behaviour of mixtures containing fatty esters, alcohols, glycerol and water is of utmost importance for the design and optimization of biodiesel purification and by-products recovery processes. In this work we show the capability of A-UNIFAC to correlate and predict the phase behaviour of these mixtures. This G^E model is an extension of UNIFAC that explicitly includes association effects between groups, based on the statistical Wertheim theory [1].

A-UNIFAC with the final set of parameters is able to predict with good agreement experimental data on binary and ternary liquid-liquid equilibria of glycerol, methanol and fatty esters as well as infinite dilution activity coefficient for these systems. Additionally, satisfactory results are obtained for the prediction of liquid-liquid equilibrium of binary mixtures containing water and fatty acid esters.

1. Introduction

Biodiesel can be prepared by transesterification of triglycerides with an excess of alcohol, to produce methyl or ethyl esters of fatty acids and glycerol. After reaction, several separation processes are required for the purification of biodiesel and the recovery of by-products.

Knowledge of phase equilibria of the reactive mixture comprising fatty esters, alcohols, glycerol and water is therefore essential for the design and optimization of these processes.

Considering the presence of several hydrogen bonding components, the associating A-UNIFAC activity coefficient model is applied to describe binary and ternary liquid-liquid equilibria (LLE) of glycerol, methanol and fatty acid esters mixtures, as well as LLE of water and methyl esters.

The parameterization methodology is described in section 3 and the results obtained are shown and discussed in section 4. The main conclusions are finally presented in section 5.

2. A-UNIFAC model

Mengarelli et al. [1] have proposed a modified UNIFAC model that takes into account association effects. This G^E model adds a group-contribution association term to the original UNIFAC combinatorial and residual expressions (Fredenslund *et al.*, 1975). The association term is based on Wertheim's theory for fluids with highly directed attractive forces [2]. The general expression for the association contribution to the activity coefficient is a function of the fraction of non-bonded sites in the solution (X^{A_k}) and in pure-component i ($X_i^{A_k}$)::

$$\ln \gamma_i^{assoc} = \sum_{k=1}^{NGA} \left\{ \nu_k^i \sum_{A_k} \left[\ln\left(\frac{X^{A_k}}{X_i^{A_k}} \right) + \frac{X_i^{A_k} - 1}{2} \right] + r_i \rho_k \sum_{A_k} \left(\frac{1 - X^{A_k}}{2} \right) \right\} \tag{1}$$

In this equation ν_k^i is the number of groups of type k in a molecule of component i, ρ_j represents the density of associating group k in the mixture and r_i represents the UNIQUAC molecular volume of species i (evaluated from UNIFAC group volume parameters R_k in the usual way; i.e. summation over all NG groups within molecule i: $r_i = \sum_{k=1}^{NG} \nu_k^i R_k$). The summation in eq. (1) extends to all NGA associating groups and A_k associating sites.

The fraction of non-bonded sites X^{A_k} is a function of the associating group density ρ_j and the association strength $\Delta^{A_k B_j}$ between site A of group k and site B of group j. This fraction is given by the following expression [1]:

$$X^{A_k} = \frac{1}{1 + \sum_{j=1}^{NGA} \sum_{B_j} \rho_j \Delta^{A_k B_j} X^{B_j}} \tag{2}$$

A similar equation is applied to caculate the fraction of non-bonded sites in pure component i:

$$X_i^{A_k} = \frac{1}{1 + \sum_{j=1}^{NGA} \sum_{B_j} (\rho_j)_i \Delta^{A_k B_j} X_i^{B_j}} \tag{3}$$

In these equations ρ_j and $(\rho_j)_i$ represent the density of associating group j in the mixture and in pure associating component i, respectively, evaluated through the value of the UNIQUAC molecular volume of specie i:

$$\rho_j = \frac{\sum_{i=1}^{NC} \nu_j^i x_i}{\sum_{i=1}^{NC} r_i x_i} \tag{4}$$

$$(\rho_j)_i = \frac{\nu_j^i}{r_i} \tag{5}$$

where x_i is the mole fraction of component i in the mixture. The densities calculated by the last equations are dimensionless and characterize the concentration of associating group j in the solution and in pure component i.

The association strength $\Delta^{A_k B_j}$ is a function of two association parameters: the energy ($\varepsilon^{A_k B_j}$) and volume ($\kappa^{A_k B_j}$) of association.

$$\Delta^{A_k B_j} = \kappa^{A_k B_j} [exp(\varepsilon^{A_k B_j} / kT) - 1] \tag{6}$$

3. Model Parameterization

3.1 Association parameters

Association effects in methanol, water and glycerol are represented by the same hydrogen-bonding hydroxyl group (OH) having two associating sites (one electronegative O and one electropositive H). There is one associating group in methanol and water and three in glycerol. Group CCOO in fatty esters can cross-associate with the electropositive site of the hydroxyl OH group.

The values for the hydroxyl (OH) and ester (CCOO) self- and cross-association parameters were already available [3] and are presented in Table 1.

Table 1. Energy ϵ/k and volume κ association parameters for the A-UNIFAC model [3]

	ϵ/k (K)	κ
Self-association OH	3125.0	0.0062
Cross-association OH – CCOO	1975.0	0.071

3.2 Residual interaction parameters

The introduction of an association contribution to the activity coefficient, makes it necessary to determine a new set of parameters for the interaction between associating and non-associating functional groups.

The residual parameters for the interactions between water and ester functional groups were previously estimated using low-pressure VLE data and infinite dilution activity coefficienta γ^{∞} in binary mixtures of esters and water [3].

For the quantification of the residual non-idealities, both methanol and glycerol molecules are represented by the molecular groups CH_3OH and $C_3H_8O_3$. The residual interaction parameters between CH_3OH and $C_3H_8O_3$ were obtained by fitting isothermal liquid-liquid equilibrium data on the ternary system dodecanoic acid methyl ester-methanol–glycerol [4].

The glycerol/paraffin ($C_3H_8O_3/CH_2$) and glycerol/ester ($C_3H_8O_3$/CCOO) interaction parameters were estimated from experimental data on liquid-liquid equilibria and γ^{∞} of the binary systems dodecanoic acid methyl ester (DAME)-glycerol and hexanoic acid methyl ester (HAME)-glycerol in the range of 320 K to 438 K [4].

The residual group interaction parameters used in this work are reported in Table 2.

Table 2. Residual group interaction parameters $a_{m,n}$ (K) for the A-UNIFAC model

	n				
m	CH_2	$C_3H_8O_3$	CH_3OH	CCOO	H_2O
CH_2	0.0	101.5[c]	122.7[b]	232.1[a]	380.5[b]
$C_3H_8O_3$	-51.2[c]	0.0	-193.6[e]	886.3[c]	n.a.
CH_3OH	-19.78[b]	427.6[e]	0.0	200.2[d]	-167.6[b]
CCOO	114.8[a]	20.0[c]	18.49[d]	0.0	-72.73[b]
H_2O	136.8[b]	n.a.	251.2[b]	150.3[b]	0.0

a: original UNIFAC parameters [5]; b: [3]; c: [6]; d: [7]; e: this work; n.a.: not available.

4. Results and discussion

In this section several correlation and prediction results are presented.

4.1 Binary systems of esters and water

An important biofuel quality parameter is its maximum water content. Thus, the correct description of the solubility of water in fatty acid esters is of major importance during production and storage of biodiesel.

The A-UNIFAC model has been previously applied to describe low pressure VLE data and γ^{∞} of binary systems of water and short-chain esters [3]. In this work the same association and residual parameters are used to predict liquid-liquid equilibrium of water and several fatty acid esters. Figures 1 and 2 show that A-UNIFAC predictions are in good agreement with the experimental information available.

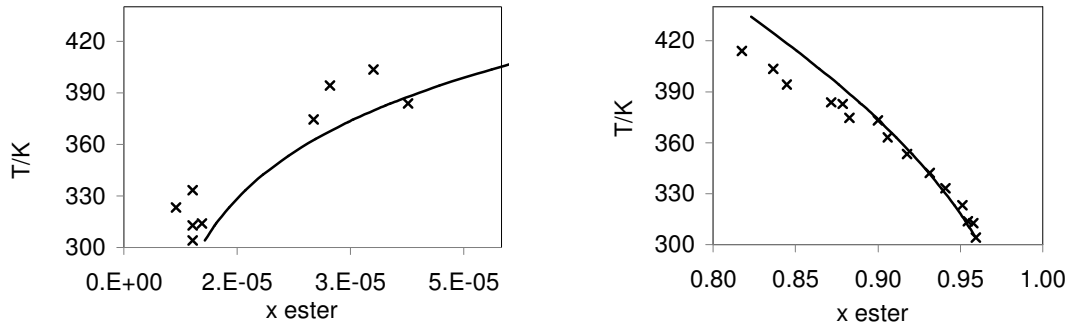


Figure 1. Liquid-liquid equilibrium of octanoic acid methyl ester + water: A-UNIFAC predictions (solid lines) and experimental data (symbols) [4].

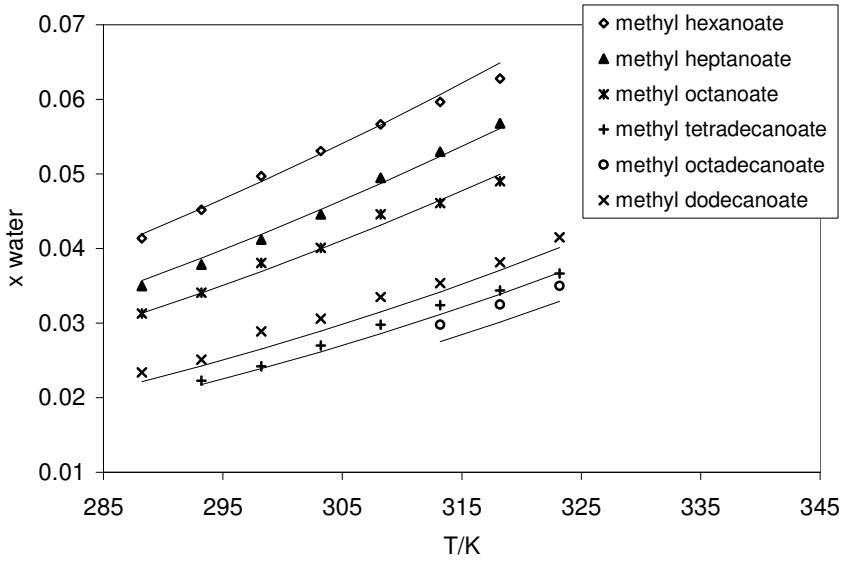


Figure 2. Water solubility in several fatty methyl esters: A-UNIFAC predictions (solid lines) and experimental data (symbols) [8].

4.2 Binary systems of esters and glycerol

Figures 3-8 compare experimental data [4] with A-UNIFAC correlation of liquid-liquid equilibrium and infinite dilution activity coefficients of the system ester / glycerol.

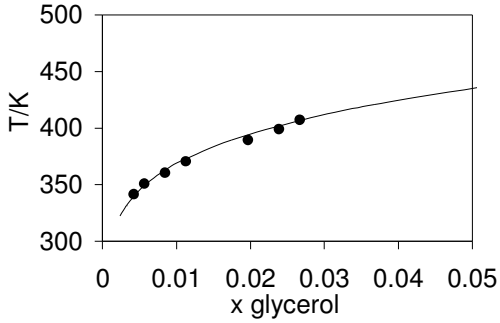


Figure 3. Comparison between A-UNIFAC correlated (solid lines) and experimental (symbols) solubility of glycerol in HAME phase.

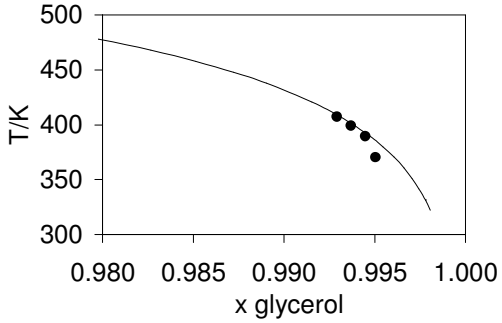


Figure 4. Comparison between A-UNIFAC correlated (solid lines) and experimental (symbols) solubility of HAME in glycerol phase.

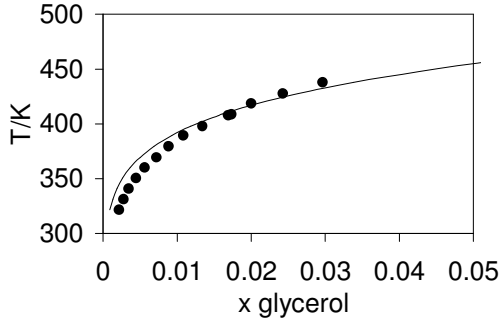


Figure 5. Comparison between A-UNIFAC correlated (solid lines) and experimental (symbols) solubility of glycerol in DAME phase.

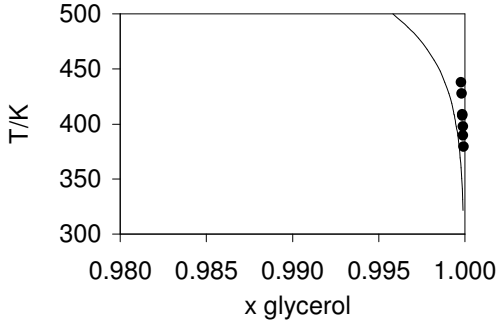


Figure 6. Comparison between A-UNIFAC correlated (solid lines) and experimental (symbols) solubility of DAME in glycerol phase.

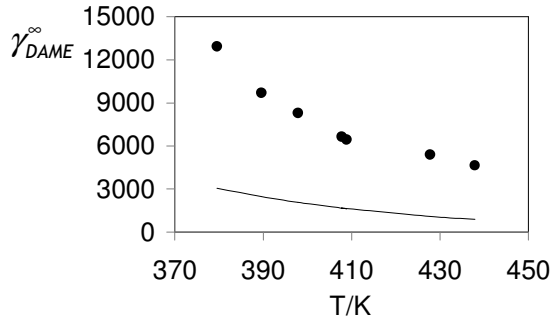


Figure 7. Comparison between A-UNIFAC correlated (solid lines) and experimental (symbols) infinite dilution activity coefficients of DAME in glycerol.

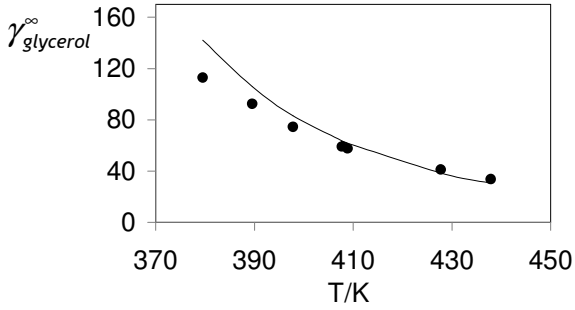


Figure 8. Comparison between A-UNIFAC correlated (solid lines) and experimental (symbols) infinite dilution activity coefficients of glycerol in DAME.

4.3 Ternary systems of esters, methanol and glycerol

The A-UNIFAC model with the parameters listed in Tables 1 and 2 was used to calculate the fluid phase equilibrium boundaries of fatty acid methyl ester-methanol-glycerol mixtures at several temperatures [4,6].

Table 3 reports the mean standard deviations in the calculation of methanol distribution coefficients by the A-UNIFAC model. The distribution coefficient $K_{methanol}$ was defined as the ratio between the methanol mole fraction in the fatty acid methyl ester and glycerol phases. Table 4 gives the mean and maximum absolute differences between calculated and experimental molar fractions of glycerol in the fatty ester phase and molar fractions of fatty ester in the glycerol phase.

Table 3. Mean standard deviations in the calculation of methanol distribution coefficients by the A-UNIFAC model

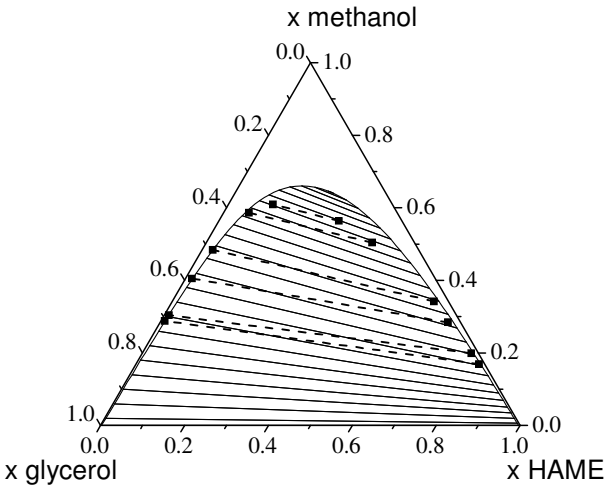
System	Standard Deviations % (*)
HAME – glycerol – methanol	12.73
DAME – glycerol – methanol	6.13
Methyl oleate (MO) – glycerol – methanol	16.36

(*) $Std.Dev.\% = 100 \times \sqrt{\sum_i \left[\left(X_{exp,i} - X_{calc,i}\right)/X_{exp,i}\right]^2 / NP}$; NP = number of experimental points

Table 4. Absolute deviations between calculated and experimental mole fractions of diluted components using A-UNIFAC

System	Mol fraction of glycerol in the fatty ester rich phase		Mol fraction of fatty ester in the glycerol phase	
	Mean difference	Maximum difference	Mean difference	Maximum difference
HAME + methanol + glycerol	0.0384	0.1064	0.0084	0.0368
DAME + methanol + glycerol	0.0179	0.0388	0.0080	0.0154
MO + methanol + glycerol	0.0050	0.0381	0.0056	0.0111

Figures 9 to 12 compare experimental data with A-UNIFAC calculations.



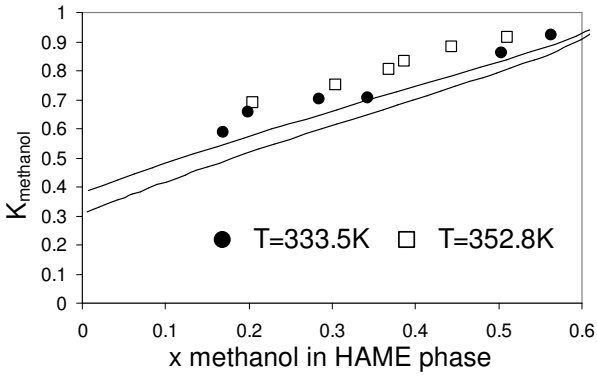
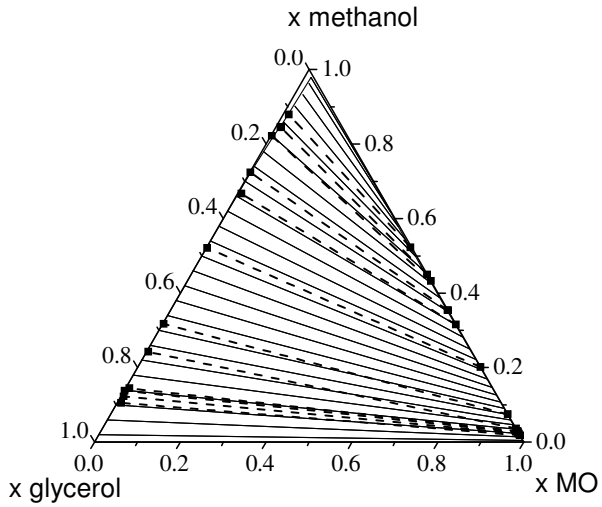


Figure 9. Comparison between A-UNIFAC predicted (solid lines) and experimental (dashed lines) [4] tie-lines of the ternary system HAME-methanol-glycerol at 333.5 K.

Figure 10. Comparison between A-UNIFAC predicted (solid lines) and experimental (symbols) [4] distribution coefficients of methanol in ternary system HAME-methanol-glycerol.



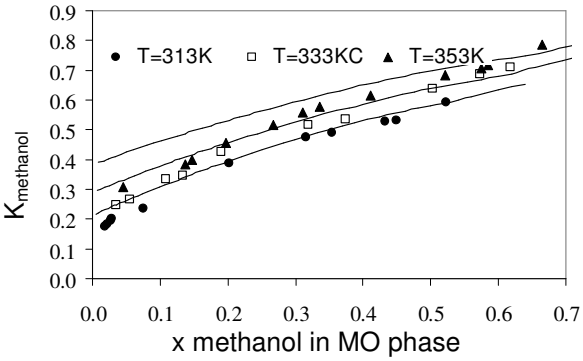


Figure 11. Comparison between A-UNIFAC predicted (solid lines) and experimental (symbols) [6] distribution coefficients of methanol in ternary system MO-methanol-glycerol at 313.15 K.

Figure 12. Comparison between A-UNIFAC predicted (solid lines) and experimental (symbols) [6] distribution coefficients of methanol in ternary system MO-methanol-glycerol.

5. Conclusions

The A-UNIFAC model gives a good representation of the liquid-liquid equilibria of mixtures containing glycerol, methanol and fatty esters as well as infinite dilution activity coefficients in these systems. This group-contribution model can be further extended to describe the phase equilibria of multicomponent mixtures of interest in biodiesel production.

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